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| 13. ABSTRACT (Maximum 200 Words) This report summarizes the results from a 3-year research program aimed at developing a basic understanding of the microstructural design, fabrication, and properties of multilayered zirconia-based composites with high toughness and oxidation resistance. Most of the effort focused on multilayered composites of Ce-ZrO ₂ and Al ₂ O ₃ which have strongly bonded interfaces. The design of the layered composite microstructure was based on micromechanics analysis: the layers modify the shape and extent of a crack tip transformation zone, leading to toughnesses over 20 MPa.m ^{1/2} . Optimum layer thicknesses were determined and related to effects of autocatalytic transformation and crack tip advance mechanisms. Crack resistance curves were measured at various temperatures: the very high toughnesses (> 10 MPa.m ^{1/2}) were limited to temperature range of ~ 100°C above the Ms temperature for the martensitic transformation. A preliminary study of multilayered composites containing weakly bonded layers (which achieve toughening by debonding) indicated that rare earth phosphates (LaPO ₄ and CePO ₄) are potentially suitable layers for Y- and Ce-stabilized zirconia composites. DTIC QUALITY INSPECTED 5 | | | | | |
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1.0 Completed Project Summary

Title: Transformation Toughening of Ceramics

Principal Investigator: Dr. D.B. Marshall

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Contract Number: F49620-92-C-0028

Senior Research Personnel: Dr. D.B. Marshall, Dr. P.E.D. Morgan, Dr. R.M. Housley, Dr. M. Dadkhah and Dr. D.R. Mumm.

Junior Research Personnel: Dr. M.C. Shaw (while working on this project was employed at Rockwell and was also a part-time graduate student at the University of California, Santa Barbara; graduated 1994), Mr. E. Wright, Mr. J.J. Ratto, Ms. A. Taylor, Mr. E. Grethel and Ms. J. Dever (the last three were students under the Rockwell Youth Motivation Program).

Publications:

1. "Recovery of Crack Tip Transformation Zones in Zirconia after High Temperature Annealing," M.C. Shaw, D.B. Marshall, A.H. Heuer and E. Inghels, *J. Am. Ceram. Soc.*, **75**[2] 474-476 (1992).
2. "The Design of High Toughness Laminar Zirconia Composites," D.B. Marshall, *Bull. Am. Ceram. Soc.*, **71**[6] 969-973 (1992).
3. "Transformation Zone Shape Effects on Crack Shielding in Ceria-Partially-Stabilized Zirconia (Ce-TZP)-Alumina Composites," C.-S. Yu, D. Shetty, M.C. Shaw and D B. Marshall, *J. Am. Ceram. Soc.*, **75**[11] 2991-2994 (1992).

4. "Indentation Studies on Y_2O_3 -Stabilized ZrO_2 : I Development of Indentation-Induced Cracks," M.S. Kaliszewski, G. Behrens, et al., *J. Am. Ceram. Soc.*, **77**[5] 1185–1193 (1994).
5. "Crack Resistance Curves in Layered Ce- ZrO_2/Al_2O_3 Ceramics," D.B. Marshall and J.J. Ratto, pp 517–523 in *Science and Technology of Zirconia V*. Eds S.P.S. Badwal, M.J. Bannister and R.J.H. Hannink, Technomic Pub. Co., 1993.
6. "Fatigue Crack Growth and Stress Redistribution at Interfaces," M.C. Shaw, D.B. Marshall, B.J. Dalgleish, M.S. Dadkhah and A.G. Evans, *Acta Met.*, **42**[12] 4091–4099 (1994).
7. "Debonding in Multilayered Composites of Zirconia and $LaPO_4$," D.B. Marshall and P.E.D. Morgan, *J. Amer. Ceram. Soc.*
8. "Damage Accumulation and Cyclic Fatigue in Mg-PSZ at Hertzian Contacts," A. Pajares, L. Wei, B.R. Lawn and D.B. Marshall, *J. Mat. Res.*, (submitted).
9. "Temperature Dependence of Toughening in Layered Zirconia Composites," M.C. Shaw, D.R. Mumm and D.B. Marshall, for *J. Am. Ceram. Soc.*
10. "Crack Growth Mechanisms in Laminar Zirconia Composites," D.B. Marshall, for *J. Am. Ceram. Soc.*
11. "Mechanisms of Toughness Enhancement in Zirconia-Based Laminar Composites," D.B. Marshall, M.C. Shaw and D.R. Mumm, for *J. Am. Ceram Soc.*
12. "Hardness-Size Effects in Multilayered Al_2O_3/ZrO_2 Composites," D.R. Mumm and D.B. Marshall for *J. Am. Ceram Soc.*
13. "Residual Stresses in Laminar Al_2O_3/ZrO_2 Composites," D.B. Marshall, for *J. Am. Ceram. Soc.*

Patent:

"Partially Stabilized ZrO_2 -based Laminar Ceramic Composites," D.B. Marshall, J.J. Ratto and F.F. Lange, U.S. Patent No. 5,284,698 (1994).

Abstract of Objectives and Accomplishments

The overall goal of this research was to generate a basic scientific understanding needed to develop high-toughness, oxidation-resistant composites based on zirconia. The specific objectives were: (1) to develop an understanding of factors that dictate the toughening of multilayered zirconia-based composites; (2) to provide a background of theoretical modeling and critical micromechanical measurements that will allow design of optimum microstructures as new material systems emerge; and (3) to develop the fabrication techniques needed to produce novel microstructures suggested by the theoretical modeling.

A major part of the research involved studies of layered composites of alumina and zirconia. In these composites, which were designed from predictions of our micromechanics modeling of transformation toughening in zirconia, the role of the alumina layers is to interrupt the autocatalytic transformation, and beneficially modify the shape of the crack-tip transformation zone. This toughening mechanism has resulted in toughnesses over $20 \text{ MPa}\cdot\text{m}^{1/2}$ in multilayered $\text{Ce-ZrO}_2/\text{Al}_2\text{O}_3$ composites. Measurements and observations from in situ mechanical testing and Raman spectroscopy, using a range of composites that were fabricated with controlled variations of microstructure, yielded the following main conclusions: (1) the optimum layer thicknesses are between about 5 and 20 times the grain size (~ 15 and $60 \mu\text{m}$ for transformable Ce-ZrO_2); (2) the peak toughness can be limited by defects in the nontransforming layer via a transition in crack tip growth mechanism (a map defining this transition was developed); (3) the very high toughnesses ($> 10 \text{ MPa}\cdot\text{m}^{1/2}$) are limited to a relatively narrow temperature range, within $\sim 100^\circ\text{C}$ above the temperature at which spontaneous martensitic transformation occurs.

An alternative approach for toughening brittle composites is to introduce interfaces or layers that debond when intercepted by a crack (interfaces in the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ layered composites are strong and showed no evidence of debonding). Following our discovery in another program that LaPO_4 forms a weak interface with Al_2O_3 , we explored the bonding and stability of LaPO_4

with several ZrO_2 systems, with the possibility in mind of combining toughening due to transformation and debonding. Multilayered composites were fabricated with alternating layers of LaPO_4 and ZrO_2 that was partially stabilized with either CeO_2 or Y_2O_3 , or with 2-phase Al_2O_3 - ZrO_2 layers. Debonding and distributed damage were observed in all cases. The LaPO_4 and Y_2O_3 -stabilized ZrO_2 layers were stable in air, with no interdiffusion detected at temperatures up to 1600°C . However, in the CeO_2 -stabilized system, interdiffusion of Ce and La occurred, leading to formation of (Ce, La) magnetoplumbites. The results suggest that CePO_4 may be a better interlayer for CeO_2 -stabilized zirconia.

The role of the interface in redistributing stress around cracks in multilayered composites with alternating brittle and ductile components was investigated. The validity of models for the role of debonding and slip on stress redistribution was examined by comparing predictions with stresses measured by fluorescence spectroscopy. Debonding was substantially more effective than slip at reducing the stress. Under fatigue loading of these composites, two competing mechanisms were observed: mixed mode cracks extended along the metal/ceramic interfaces normal to the tip of the main crack (thus reducing the stresses ahead of the crack); while intact metal ligaments bridging the crack ruptured rapidly by Mode I fatigue crack growth (thus increasing the crack tip stress). This duality in fatigue behavior might be exploited to optimize the fatigue resistance of metal ceramic multilayers.

Substantial effort was also devoted to improving fabrication methods for the multilayered ceramic composites developed under this program. The sequential centrifuging method developed in this contract to consolidate slurry powders is very convenient for testing new microstructures. However, in nonautomated systems it is very slow and labor-intensive, while in automated systems it would be limited mainly to axisymmetric shapes. An alternative slurry consolidation route, using the same colloidal systems but using sequential vacuum slip casting instead of centrifuging, yielded comparable results. This method can be faster for limited component thicknesses. It is also more versatile for producing more complex shapes and has potential to be adapted to rapid free-forming of complex components by laser scanning driven by a CAD file of the component. Another approach, based on tape casting instead of colloidal processing, is also under development in collaboration with two companies. In one of these collaborations, the company DSM is producing tapes of Ce-ZrO_2 and Al_2O_2 , while the consolidation and sintering conditions are being developed in collaboration with Prof. F. Lange and graduate student C. Hillman at the University of California at Santa Barbara. The other

collaboration involves Lone Peak Engineering (Utah), who are using tape-cast layers of Ce-ZrO_2 and Al_2O_3 with a "laminated object manufacturing" method in which the individual tapes are cut as they are stacked using a laser that is controlled by a CAD file to produce complex shaped components directly.

2.0 Summary of Research

2.1 Crack Resistance Curves in Layered Ce-ZrO₂/Al₂O₃ Ceramics

During the previous year, we demonstrated that very high fracture toughnesses ($\sim 18 \text{ MPa}\cdot\text{m}^{1/2}$) could be achieved in multilayered composites of Al₂O₃ and Ce-ZrO₂. These composites were designed on the basis of micromechanics modeling. The toughening is due to martensitic transformation of zirconia from the tetragonal to the monoclinic phase around cracks. The modeling predicted that with certain dual scale microstructures, the shape of the crack tip transformation zone could be modified to increase the toughening. Initial experiments indicated that, in addition to truncating the zone ahead of the crack tip as predicted, the presence of the Al₂O₃ layers caused the transformation zone in the zirconia to spread along the region adjacent to the layers, thus increasing the zone width by up to a factor of 10 and further enhancing the toughness.

To explore the influence of layer dimensions and matrix properties on the toughening, a series of composites with various layer thicknesses and with Ce-ZrO₂ materials of two different initial fracture toughnesses were fabricated. These composites contained multilayered regions embedded in uniform Ce-ZrO₂ to allow controlled crack growth experiments within both layered and nonlayered materials in the same specimen. This allowed direct measurement of the toughening due to the layers, with the assurance that all other influences were equal. The R-curve measurements were obtained using notched beams loaded in flexure, with in situ measurement of crack growth and transformation zone development. The results indicated that the toughening, and in particular the slope of the R-curve, was insensitive to the layer thicknesses in the range 20 to 70 μm , and that the toughening increased as the transformability of the Ce-ZrO₂ matrix increased.

The peak toughness in these studies, while substantially increased over that of the base material (to $18 \text{ MPa}\cdot\text{m}^{1/2}$ from $\sim 5 \text{ MPa}\cdot\text{m}^{1/2}$), was limited by the finite number of layers in the test specimens (typically 20 layers), and the limited specimen thicknesses ($\sim 6 \text{ mm}$). Substantial effort was devoted to improving the colloidal method used to fabricate the multilayered structures. The method, developed in collaboration with F.F. Lange (UC Santa Barbara), involved sequential centrifugal consolidation of the Al₂O₃ and Ce-ZrO₂ powders. The key requirements for achieving large fully dense, crack-free composites is to obtain very uniform

powder packing. Disk-shaped specimens with dimensions $\sim 70 \times 15$ mm containing ~ 300 layers were fabricated for further studies.

2.2 Mechanisms of Toughness Enhance in Zirconia-Based Laminar Composites

Two effects contribute to the large toughness enhancement in multilayered $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composites. One is a truncation of the transformation zone ahead of the crack, as predicted by our previous analysis. The other, which was not predicated, is the spreading of the zone sideways along the layers. Several factors potentially contribute to the sideways spreading: (1) the modification of stresses adjacent to the crack by the presence of a nontransforming layer; (2) further modification of these stresses by the difference in elastic modulus of the Al_2O_3 and ZrO_2 layers; or (3) residual stresses due to thermal expansion mismatch. Although substantial residual stresses exist in these composites (~ 100 MPa in composites with ZrO_2 and mixed $\text{Al}_2\text{O}_3\text{-ZrO}_2$ layers), these are thought not to be the major cause of zone spreading: the spreading was observed also in specimens containing only isolated layers of $\text{Al}_2\text{O}_3\text{-ZrO}_2$, for which the residual stress in the ZrO_2 matrix was negligible.

The influence of the first two mechanisms was assessed using a finite element analysis. The results indicated that the presence of a nontransforming layer near the crack tip causes very little change in hydrostatic stress components around the perimeter of the transformation zone, regardless of whether or not there is a difference in elastic modulus. However, the large shear stress concentration at the position where the spreading of the transformation zone was observed (Fig. 1) is consistent with the postulate that the transformation is initiated by shear. The stress concentrations were almost the same for the two cases evaluated, one with equal elastic moduli for both layers and the other with the stiffness of the nontransforming layer being double that of the transforming material, corresponding to the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ system. Therefore, the higher stiffness of the alumina layers is not an important factor.

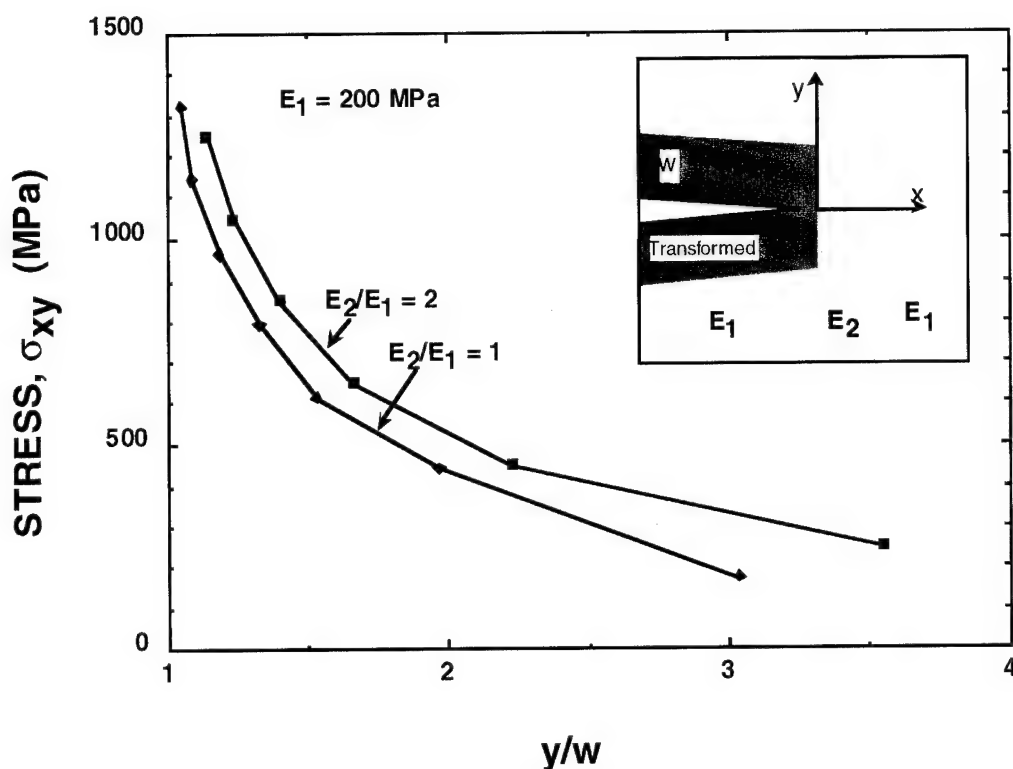


Fig. 1. Shear stress concentration adjacent to nontransforming layer ahead of crack tip in transformation toughened zirconia.

The stress concentration due to the nontransforming layer provides stresses above the known initiation stress for transformation (~ 400 MPa) over a distance about equal to the transformation zone width (Fig. 1). This indicates that the stress concentration exists over a sufficiently large volume of material to effect initiation of transformation. Once this occurs, continued growth of the transformation along the layer would be expected, because of autocatalytic effects and because the stress concentration would shift along ahead of the transformation.

2.3 Transformation Mechanisms and Optimum Layer Thicknesses in Multilayered Zirconia Composites

To investigate the effect of layer thickness on the extent of sideways spreading of the transformation zone in multilayered zirconia composites, specimens containing layers of ZrO_2

and $\text{Al}_2\text{O}_3/\text{ZrO}_2$ of various thicknesses were fabricated. This allowed investigation of relative transformation zone widths with all other experimental variables held constant.

Relative zone widths in layers of different thickness were measured under various conditions: (1) growth of cracks in notched beams, with in situ observation using high resolution Nomarski interference; (2) indentation with a Vickers indenter, and (3) controlled cooling with in situ observation by Nomarski interference. The results indicated that the extent of transformation is maximum for ZrO_2 layer thicknesses in the range ~ 15 to $70\ \mu\text{m}$ (Fig. 2), corresponding to ~ 5 to 20 times the grain size of the transforming ZrO_2 . At layer thicknesses above this range, transformation occurred in isolated bands traversing the layers as shown in Fig. 2, while at layer thicknesses below the range, the extent of transformation was less. The results were attributed to the effect of autocatalytic transformation: at layer widths below a few times the grain size the autocatalytic transformation is ineffective; while at layer thicknesses above ~ 20 times grain size, there are an excess of nucleation sites that are able to initiate separate transformation bands ahead of an advancing transformation front, which in turn cause the front to arrest.

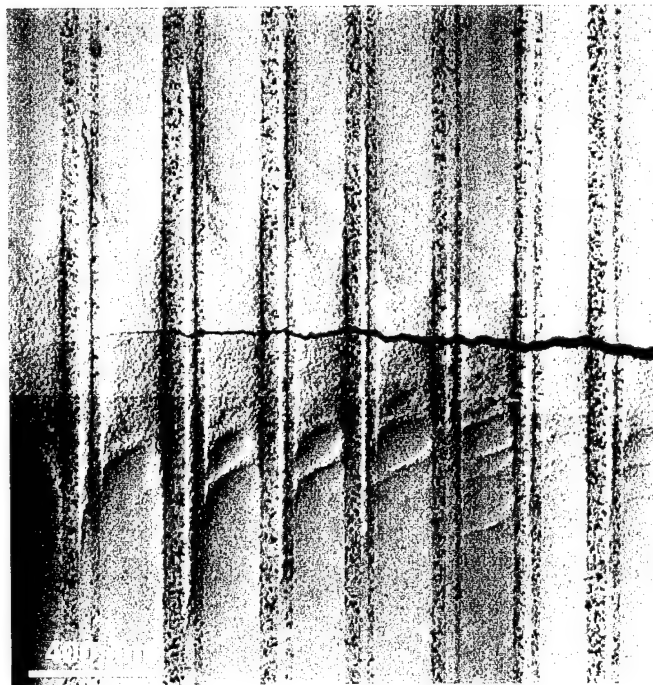


Fig. 2. Nomarski interference micrograph showing transformation zone in multilayered Ce- $\text{ZrO}_2/\text{Al}_2\text{O}_3$ composite: note more extensive transformation in narrower ZrO_2 layers ($\sim 30\ \mu\text{m}$ thickness) and banded structure in wider layers.

2.4 Crack Growth Mechanisms in Laminar Zirconia Composites

In situ observations of crack growth during R-curve measurements in $\text{Al}_2\text{O}_3/\text{ZrO}_2$ multilayered composites indicated that in some composites, cracks grew by continuous advance of the crack tip; while in others cracks initiated in Al_2O_3 layers ahead of the main crack and linked back to the main crack tip. The latter mechanism, which limits the toughness achievable, tended to occur in composites with some porosity in the Al_2O_3 layers.

The transition in cracking mechanism was modeled as a competition of tunnel cracking in the intact Al_2O_3 layer ahead of the main crack tip and direct advance of the shielded main crack tip. As the degree of toughening due to the transformation zone increases (due for example to changing test temperature or to heat treatment used to increase the transformability of the zirconia), the stress driving tunnel cracking in the Al_2O_3 layer ahead of the main crack increases. A failure map defines the transition condition (i.e., the maximum toughness) in terms of two dimensionless parameters (Fig. 3): c_0/t , the ratio of size of defects in the Al_2O_3 layers to the thickness of the ZrO_2 layers; and $\alpha = \frac{\sigma_R + \sigma_T}{\sigma_0}$ where σ_R and σ_T are the stresses in the Al_2O_3 layer due to thermal expansion mismatch and to a transformed layer of ZrO_2 , and σ_0 is the tunneling stress in the alumina layer. The results indicate that this upper bound and the toughness are increased by reducing the sizes of defects in the Al_2O_3 layers and/or reducing the Al_2O_3 layer thickness.

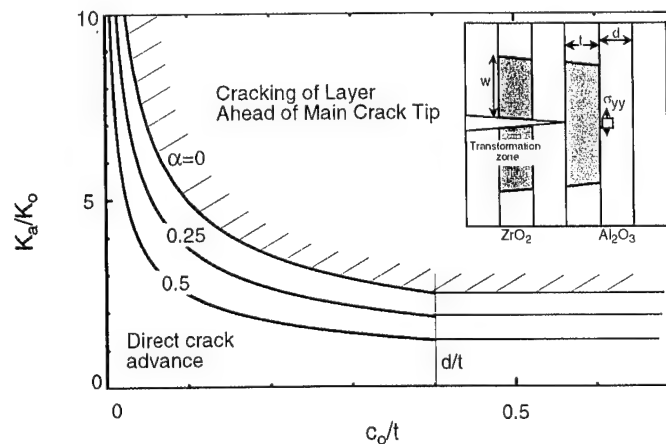
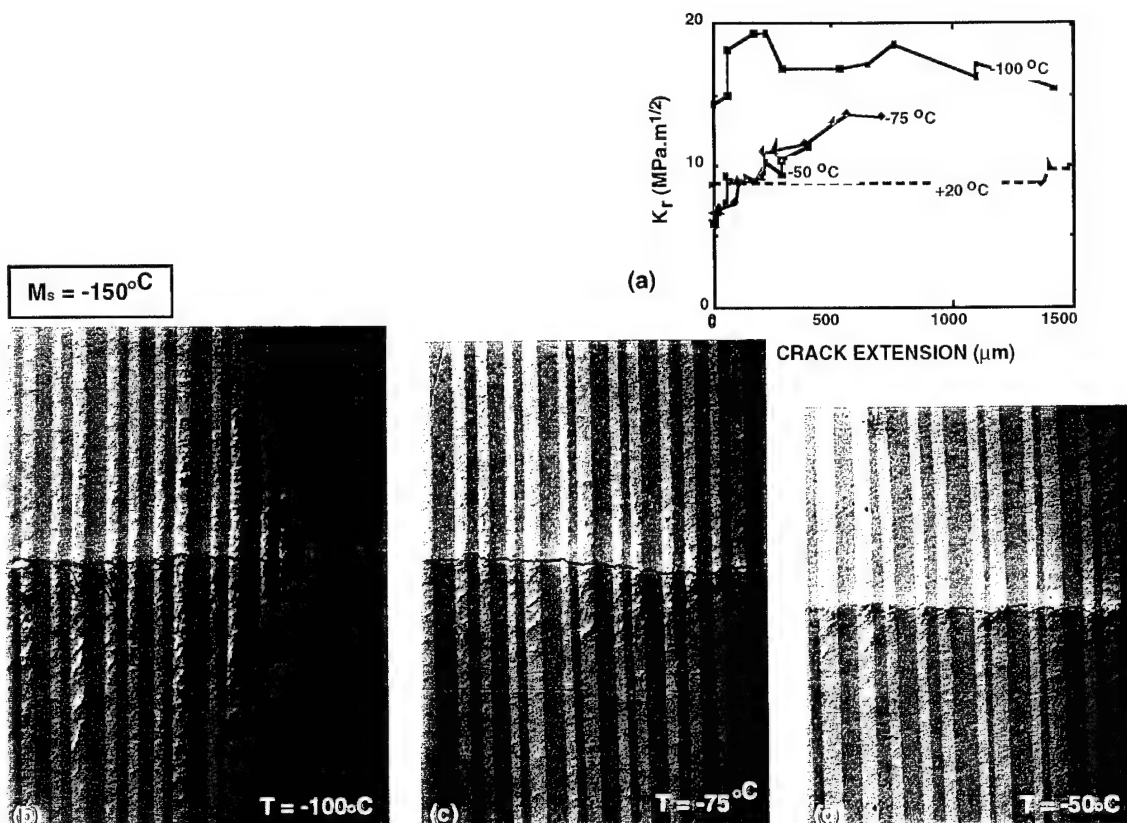


Fig. 3. Failure map showing transition in crack tip advance mechanism (which also defines the maximum toughness achievable).

2.5 Temperature Dependence of Toughening in Layered Zirconia Composites

The degree of transformation toughening in ZrO_2 materials is well-known to decrease with increasing test temperature. To measure the sensitivity of the enhanced toughening in the laminar composites to test temperature, R-curves were measured at various temperatures between the M_s temperature (the temperature at which the martensitic tetragonal-to-monoclinic transformation occurs spontaneously) and room temperature, using several different materials that had different M_s temperatures within the range 0°C and -150°C . These measurements were made using a loading fixture on the stage of an optical microscope, which allowed measurement of crack growth and transformation zone dimensions in situ. Cooling was achieved using circulating cold nitrogen.

The degree of toughening and the size of the crack tip transformation zone were very sensitive to the difference between the test temperature and the M_s temperature, as illustrated in Fig. 4. The very large transformation zones such as in Fig. 4 (b) and (c) and toughnesses above $15 \text{ MPa}\cdot\text{m}^{1/2}$ were observed only for test temperatures within about 100°C of the M_s temperature. Therefore, applications that could take advantage of the extraordinarily high toughnesses achievable in these systems would be restricted.



4. Temperature dependence of toughening in multilayered $\text{Ce-ZrO}_2/\text{Al}_2\text{O}_3$ composite:
 (a) Crack resistance curves measured at various temperatures.
 (b) – (d) Nomarski interference micrographs showing transformation zones from specimens in (a).

2.6 Hardness-Size Effects and Residual Stresses in Multilayered $\text{ZrO}_2/\text{Al}_2\text{O}_3$ Composites

Contact damage pertinent to wear and abrasion in multilayered $\text{Ce-ZrO}_2/\text{Al}_2\text{O}_3$ composites was assessed using Vickers indentation. For contact areas much larger than the layer thickness, the hardness was given by average of the hardnesses of the individual layers, weighted by the relative layer thicknesses. For contact areas comparable with the layer dimensions, the hardness did not scale with the relative fractions of the two layers within the contact area. Instead, it scaled with the relative volume fractions within the surrounding plastic zone. This resulted in a higher hardness than expected based on contact area for contact sites centered in the softer ZrO_2 layers and lower hardness for those centered in the harder Al_2O_3 layers.

Residual stresses due to thermal expansion mismatch in multilayered composites containing layers of Y-ZrO₂ and Al₂O₃-ZrO₂ were detected via their influence on Vickers indentation cracks. The results confirmed expected trends: parallel to the layers, the thermal mismatch generated tension in the ZrO₂ layers and compression in the Al₂O₃ layers; whereas normal to the layers, surface effects generated tension in the Al₂O₃ layers and compression in the ZrO₂ layers.

2.7 Indentation Studies of Y₂O₃-Stabilized ZrO₂

Cracks induced by indentation with a Vickers indenter are commonly used for measurement of fracture toughness in ceramics, including transformation toughened zirconia. However, the strains associated with the tetragonal-to-monoclinic transformation at the indentation side are not accounted for in previous analyses used to calculate the toughness. A study was undertaken to assess the amount of transformation induced by indentation and its influence on the evolution of the cracks, the crack shape and toughness measurements. The analysis of indentation cracking that is used to evaluate fracture toughness was revised to account for the presence of transformation strain. This work was done in collaboration with Prof. A.H. Heuer and Ms. M.S. Kaliszewski at Case Western Reserve University, as well as several others listed as co-authors on the paper of the same title listed in Section 1. Ms. Kaliszewski, a graduate student, visited Rockwell Science Center to perform some of her experimental work.

2.8 Damage Accumulation and Cyclic Fatigue in Mg-PSZ at Hertzian Contacts

Irreversible damage caused by Hertzian contact (monotonic and cyclic) in three Mg-PSZ materials that had been heat-treated to different states was investigated. Analytical techniques, including optical and scanning electron microscopy, acoustic emission, Raman spectroscopy and thermal wave imaging, showed that the damage mechanisms were fundamentally different in three aging states. The dominant damage mechanisms were: microfracture in as-fired material (material in which tetragonal precipitates are not easily transformed to the monoclinic phase); tetragonal-to-monoclinic transformation in peak aged material (material of highest toughness, in which tetragonal precipitates are easily transformed); and monoclinic phase twinning in over-aged material (material in which most precipitates are already transformed from the tetragonal to the monoclinic phase). This work was done in collaboration with the group at NIST led by Dr. B.

Lawn; Dr. A. Pajares, a visiting scientist, spent time at Rockwell Science Center performing Raman spectroscopy and optical microscopy.

2.9 Debonding in Multilayered Composites of Zirconia and LaPO_4

An alternative approach to transformation toughening for toughening brittle composites is to introduce interfaces or layers that debond when intercepted by a crack (interfaces in the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ layered composites are strong and showed no evidence of debonding). This mechanism has the advantage that it is not temperature sensitive as is the transformation mechanism; but the disadvantage that weak interfaces lead to low transverse strength. Following our discovery in another program that LaPO_4 forms a weak interface with Al_2O_3 , we explored the bonding and stability of LaPO_4 with several ZrO_2 systems, with the possibility in mind of combining toughening due to transformation and debonding. Multilayered composites were fabricated with alternating layers of LaPO_4 and ZrO_2 that was partially stabilized with either CeO_2 or Y_2O_3 , or with 2-phase $\text{Al}_2\text{O}_3\text{-ZrO}_2$ layers. Debonding and distributed damage was observed in all cases (Fig. 5). The LaPO_4 and Y_2O_3 -stabilized ZrO_2 layers were stable in air, with no interdiffusion detected at temperatures up to 1600°C . However, in the CeO_2 -stabilized system, interdiffusion of Ce and La occurred, leading to formation of (Ce, La) magnetoplumbites. The results suggest that CePO_4 may be a better interlayer for CeO_2 -stabilized zirconia.

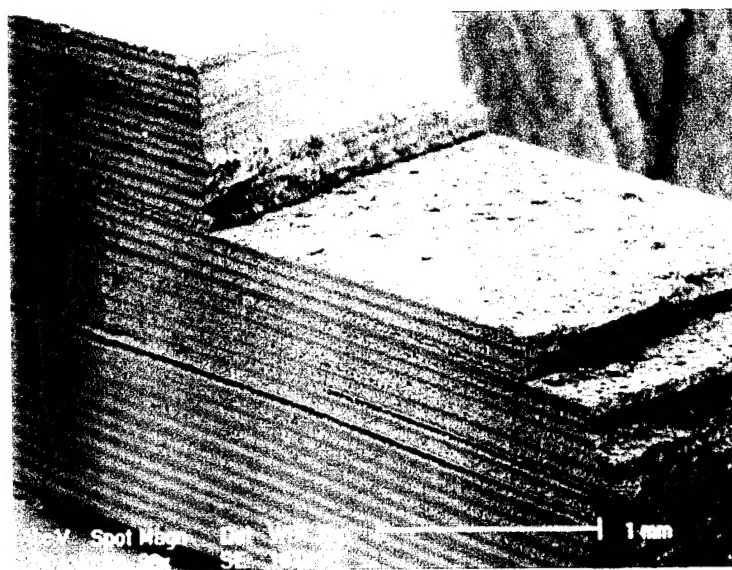


Fig. 5. Broken beam of multilayered $\text{Ce-ZrO}_2/\text{LaPO}_4$, showing delamination at LaPO_4 layers.

2.10 Fatigue Crack Growth and Stress Redistribution at Interfaces

The role of the interface in redistributing stress around cracks in multilayered composites with alternating brittle and ductile components was investigated. The validity of models for the role of debonding and slip on stress redistribution was examined by comparing predictions with stresses measured by fluorescence spectroscopy. Debonding was substantially more effective than slip at reducing the stress. Under fatigue loading of these composites, two competing mechanisms were observed: mixed mode cracks extended along the metal/ceramic interfaces normal to the tip of the main crack (thus reducing the stresses ahead of the crack); while intact metal ligaments bridging the crack ruptured rapidly by Mode I fatigue crack growth (thus increasing the crack tip stress). This duality in fatigue behavior might be exploited to optimize the fatigue resistance of metal ceramic multilayers. This work was done as part of the Ph.D. thesis of Dr. M.C. Shaw, in collaboration with Prof. A.G. Evans at the University of California, Santa Barbara, while Dr. Shaw was employed at Rockwell. The experimental work was done at Rockwell Science Center.

3.0 Transition of Accomplishments to Industry

We are collaborating with two companies to examine the feasibility of producing multilayered components based on the composites developed in this program. Tape-casting fabrication methods are being developed because of their potential versatility for producing shaped components. One company, DSM, is producing tapes of Ce-ZrO₂ and mixed Ce-ZrO₂/Al₂O₃, while the consolidation and sintering conditions are being developed in collaboration with Prof. F. Lange and graduate student C. Hillman at the University of California at Santa Barbara. The other company, Lone Peak Engineering (Utah), are using tape-cast layers of Ce-ZrO₂ and Al₂O₃/Ce-ZrO₂ with a "laminated object manufacturing" method, in which the individual tapes are cut as they are stacked using a laser that is controlled by a CAD file; this method produces complex shaped components directly from a series of slices from the computer file of the component. They have achieved dense multilayered microstructures with toughnesses of 10 MPa.m^{1/2} and strengths of 700 MPa, a significant improvement over monolithic Ce-ZrO₂ or Al₂O₃ fabricated by the same method (strength 540 MPa, toughness 6.7 MPa).

Rockwell's Rocketdyne Division are assessing the feasibility of a graded Al₂O₃-ZrO₂ composite rocket engine injector that would be fabricated using a free-form method; either the LOM method being developed by Lone Peak Engineering, or a colloiddally-based laser sintering method that we are exploring separately. Rockwell are also investigating 3-D photonic band gap structures that incorporate these materials with complex shapes produced by Lone Peak Engineering's laminated object manufacturing method.